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Nucleus-Coupled Electron Transfer Mechanism for TiO2-Catalyzed Water Splitting[1] YIYANG SUN, MICHAEL LUCKING, DAMIEN WEST, SHENGBAI ZHANG, Rensselaer Polytechnic Institute — Using first-principles calculations employing explicit interface of TiO_2 crystal and liquid water, we reveal the microscopic mechanism of the oxygen evolution reaction (OER). It is found that, during the formation of an O–O species, such as HO–OH and O–OH, an occupied molecular orbital with anti-bonding character evolves from the valence band and pops up all the way into the conduction band of TiO_2. This occupied high-energy orbital results in a high reaction barrier making the OER forbidden in the dark. The presence of photoholes depletes this anti-bonding orbital, which significantly reduces the reaction energy and determines the reaction barrier in the rate-limting step. A novel reaction mechanism, termed necleus-coupled electron transfer (NCET), emerges from this study. In this mechanism, the oxidation of a pair of hydroxyl groups, which is an electron transfer reaction, is enabled by the movement of the nuclei (i.e., the two O atoms moving towards O-O bond formation) that pushes the *reactive* orbital (the σ_{2p}^* orbital in the present case) to become the $frontier$ orbital (i.e., above the valence band maximum of TiO). Based on the NCET mechanism, we identify a reaction pathway of the OER that exhibits a kinetic barrier surmountable at room temperature.

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Yiyang Sun
Rensselaer Polytechnic Institute

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